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(54) Title: APPARATUS AND METHOD FOR CLEANING WASTE WATER AND WASTE SLUDGE BY MEANS OF ION EXCHANGERS

(57) Abstract

The invention relates to a device for cleaning waste water or waste slurry by means of ion exchangers held on carriers, comprising: a container; feed means for feeding the waste water for cleaning to the container; carrier feed means for feeding carriers provided with ion exchangers to the container; an agitation device arranged in the container; and a separating device connected to the container by means of a pipe for separating the carriers from the waste water. As a result of these steps the carriers of the ion exchangers are carried suspended or floating into the water, so that the danger of blockage is avoided. The separating device prevents the ion exchangers being discharged together with the waste water that has meanwhile been cleaned. This separating device can be formed by a filter, for example, a mechanical or an electrostatic filter, but can likewise be formed by a magnetic separating device. The carriers must then of course be magnetic.

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APPARATUS AND METHOD FOR CLEANING WASTE WATER AND WASTE SLUDGE BY MEANS OF ION EXCHANGERS

The present invention relates to a device for cleaning waste water by means of ion exchangers held on carriers.

Such devices are generally known.

With such known devices the ion exchangers are held on carriers, which carriers are placed together into a container, and wherein the waste water for cleaning is guided through the container. The waste water for cleaning herein flows into the pores which are formed by the spaces between the carriers, so that the waste water for cleaning comes into intensive contact with the walls of the carriers.

Although such carriers operate well in removing the waste products from the water, such devices operate badly with turbid waste water; due to solid substances present in suspension or otherwise floating or formed in the waste water, this device becomes blocked so that it becomes inoperative.

The object of the present invention is to provide a device which also operates well in the case of turbid waste water and remains operative.

This object is achieved in that the device comprises: a container; feed means for feeding the waste water for cleaning to the container; carrier feed means for feeding carriers provided with ion exchangers to the container; an agitation device arranged in the container; and a separating device connected to the container by means of a pipe for separating the carriers from the waste water.

As a result of these steps the carriers of the ion exchangers are placed suspended or floating in the water, so that the danger of blockage is avoided. The separating device prevents the ion exchangers from being discharged together with the waste water that has meanwhile been cleaned.

This separating device can be formed by a filter, for example a mechanical or an electro-static filter, but is

preferably formed by a magnetic separating device. The carriers must then of course be magnetic.

According to a preferred embodiment the device for cleaning waste water is formed by at least two devices connected in series as claimed in claim 1 or 2, wherein the carrier feed means are adapted for feeding the carriers provided with ion exchangers to the second container in the flow direction, wherein the second separating device in downstream direction is adapted for feeding the separated carriers provided with partially used up ion exchangers to the first container in the flow direction, and wherein the first separating means in the flow direction is adapted for discharging the carriers provided with used up ion exchangers.

In this preferred embodiment of the invention particularly effective use is made of the ion exchangers; the already used ion exchangers come into contact with the most contaminated water, while the water already somewhat cleaned water comes into contact with fresh ion exchangers, so that these can remove the last remnants of the substances for removing from the water.

This device is particularly suitable for removing metals from waste water.

A problem which is typical for the treatment of waste water, whether of an industrial or domestic nature, is the greatly varying and often unpredictable flow rate and the greatly varying and likewise poorly predictable degree of contamination. The invention offers a solution for this problem in that the carriers can be magnetized and the separating device is a magnetic separating device. This offers the possibility of adapting the amount of supplied carriers to the flow rate of waste water for cleaning and the degree of contamination.

In addition to the described two-stage embodiment this device can of course likewise be applied in a multi-stage embodiment.

The present invention will subsequently be elucidated with reference to the annexed drawings, in which:

fig. 1 shows a schematic perspective view of a first embodiment of the present invention;

fig. 2 is a schematic perspective view of a second embodiment of the invention; and

fig. 3 is a schematic perspective view of a third embodiment of the invention.

A feed pipe 2 with which the waste water for cleaning is fed debouches into the container 1. A feed pipe 3 for feeding carriers provided with ion exchangers further debouches into the container 1.

Arranged in container 1 is an agitation device 4 formed by a motor 5 which is fixed onto a connecting beam 6 arranged in container 1 and which drives an agitation blade 8 by means of a shaft 7.

A discharge pipe 9 leads from container 1 to a magnetic separating device 10. From the magnetic separating device 10 a discharge pipe 11 leads to a pump 12 with which the cleaned waste water is drained. The separating device 10 is of the type as described in the Dutch patent application 8801463.

A discharge pipe 13 for separated carriers is connected to the separating device 10, which pipe 13 leads to a schematically depicted regeneration device 14. From the regeneration device 14 a pipe 15 leads to a storage container 16 in which the regenerated carriers 17 are stored. From the storage container the feed pipe already indicated leads to container 1. A closing valve 18 is otherwise arranged in the pipe 3.

The action of this device is such that the waste water for cleaning, which can be turbid, is fed to the container 1. The device according to the invention will otherwise also operate well with clear, that is non-turbid, waste water. The carriers 17 provided with ion exchangers by means of the pipe 3 and closing valve 18 are also supplied to the container 1. Once there the waste water for cleaning is agitated by the agitation device 4 so that an intensive contact is created between the carriers and the supplied waste water. Once the mixture of waste water and carriers has remained long enough in the container 1, the

waste water together with the carriers moving therein flows through the pipe 9 to the magnetic separating device 10. Separation of the magnetic carriers takes place there and the waste water with the magnetic carriers removed is drained by means of the discharge pipe 11 and the pump 12. This waste water is of course divested not only of the carriers but of the substances for removal taken up by the ion exchangers present on the carriers.

The carriers thus provided with these substances are fed by means of the pipe 13 to the regeneration device 14 where they are regenerated. The regenerated carriers are fed to the storage container 16 by means of the pipe 15.

It will be apparent that the device described here can be modified in various ways; for example instead of a magnetic separating device it is possible to apply another separating device, for example a mechanical filter, which must be regularly divested of carriers to prevent blockage, or for example an electro-static filter. It is important for this purpose that the carriers all have a similar electrical charge.

It is of course likewise possible to make use of other types of magnetic separating devices.

Another embodiment of the invention is now shown in fig. 2, wherein corresponding components are designated with corresponding reference numerals.

In this situation the waste water for cleaning is also fed by means of a feed pipe 2 which debouches in a first container 19. From the container 19 a pipe 20 leads to a separating device designated in its entirety by 21. The water coming from the first separating device is fed via a pipe 22, in which a pump 23 is arranged, to a second container 24. From the second container 24 a discharge pipe 25 leads to a second separating device 26. From the second separating device 26 a discharge pipe 27 leads away the cleaned waste water. A pump 28 is received in this pipe.

Carriers with regenerated ion exchangers are supplied from a storage container 16 to the container 24 by means of a pipe 3 in which a closing valve 18 is incorporated. The carriers separated in the second separating device 26

are supplied to the first container 19 by means of a pipe 29, in which for example may be arranged a pump (not shown in the drawing).

Carriers coming from the first separating device 21 are supplied by means of a pipe 30 to a regeneration device 14 from which a pipe 15 leads to the container 16.

The first and the second separation device are each provided with a housing 31 in which is situated a horizontal shaft 32 driven in rotation, whereon in the present embodiment three discs 33 provided with magnets are fixed. By means of a motor 34 fixed on the shaft the discs are driven in rotation. The mixture consisting of waste water and the carriers taken up therein is fed to the interior of the housing by means of the pipe 20. The magnetic carriers are attracted by the magnets present in discs 33, whereafter they are then scraped off by the scraping devices through rotation of the discs and by means of the ducts connected thereto fall into a collection space 37 and are then discharged through pipe 30. Such a device otherwise forms the subject of the non-prepublished Dutch patent application 9101872.

It will likewise be apparent that various modifications can also be made to the device shown here; it is possible for example instead of the two-stage device applied here to apply a three-stage device or even a device with a number of stages larger than three.

Finally, fig. 3 shows a third embodiment which is particularly suitable for processing waste water with greatly varying flow rate. This third embodiment differs from the second embodiment in that an extra storage container 40 is arranged in which a store of carriers with ion exchangers can be stored. This relates to carriers coming from the second separating device 26 which are supplied via the pipe 29 and which have thus already been "used up" to a certain degree.

This third embodiment further differs in that above the regeneration device 14 is arranged a storage container 41 fulfilling the same function; with a large feed of the waste water for cleaning the separating device will sepa-

rate a large amount of completely used up ion exchangers which must be regenerated in the regeneration device 14. With an excess of waste water for cleaning the amount fed will exceed the capacity of the regeneration device 14 so that this excess can be stored in the storage container 41. This offers the possibility of selecting a smaller capacity for the regeneration unit 14.

The device also provides for the possibility that the quality of the supplied waste water is relatively good, that is, that it is lightly contaminated. In such a situation it is possible to bypass the first stage, that is, to stop feed of carriers provided with ion exchangers from storage container 40 and to lead the waste water via the bypass pipe 42 to the container 24. It is also possible in such a situation to switch off the first separating device 21.

The above described embodiment further relates to cleaning of contaminated waste water; not only domestic, industrial or other waste water must be considered as waste water, but also other liquids from which can be removed materials removable by means of ion exchangers. The invention is, partly because of the fact that blockage is prevented, particularly suitable for cleaning liquids with particles suspended therein, even so many particles that it may be described as a slurry.

The invention offers the possibility of removing the waste products from the waste water in a manner such that neither the remaining liquid medium nor the separated product is regarded as chemical waste and can even be used as raw material.

In general ion exchangers are used for removing metals, but it would likewise be possible when suitable adsorbents become available, to apply these for removing other substances, such as organic pollutants.

Finally, an example follows of the application of a device and method according to the invention.

Waste water coming from the nickel washing baths of an enamelling plant, comprising ± 90 mg Ni/l, ± 45 mg Fe/l and 920 mg Na/l, was treated in a two-stage counterflow

system as described in figure 2. The capture of the magnetic resin took place with electromagnets. The ion exchanger used consisted of a weak acid resin with Fe_2O_3 as magnetic component. The resin is selective for the transition elements.

At an average treatment time of 15 minutes in the total system an effluent concentration of <0.5 mg/l could be achieved.

CLAIMS

1. Device for cleaning waste water or waste slurry by means of ion exchangers held on carriers, **characterized by:**

- a container;
- feed means for feeding the waste water for cleaning to the container;
- carrier feed means for feeding to the container carriers provided with ion exchangers;
- an agitation device arranged in the container; and
- a separating device connected to the container by means of a pipe for separating the carriers from the waste water.

2. Device as claimed in claim 1, **characterized in that** the carrier feed means comprise a buffer storage container.

3. Device as claimed in claim 1 or 2, **characterized in that** the carriers can be magnetized, and that the separating device is a magnetic separating device.

4. Device as claimed in claim 1, 2 or 3, **characterized in that** a regeneration device for regenerating the ion exchangers is connected to the separating device.

5. Device as claimed in claim 4, **characterized in that** the regeneration device is coupled to a buffer storage container.

6. Device for cleaning waste water, **characterized by** at least two devices connected in series as claimed in any of the claims 1-5, wherein the carrier feed means are adapted for feeding the carriers provided with ion exchangers to the second container in the flow direction; wherein the second separating device in downstream direction is adapted for feeding the separated carriers provided with partially used up ion exchangers to the first container in the flow direction, and wherein the first separating means in the flow direction is adapted for discharging the carriers provided with used up ion exchangers.

7. Device as claimed in claim 6, **characterized in that** the carriers discharged by the first separating device in flow direction are supplied to a regeneration device, and that the carriers coming from the regeneration device are supplied to the second feed means in flow direction.

8. Device as claimed in any of the foregoing claims, **characterized in that** an agitation device is arranged in one of the containers.

9. Device as claimed in any of the claims 6-8, **characterized in that** the device comprises means switching off the first cleaning device depending on the degree of contamination of the waste water for cleaning.

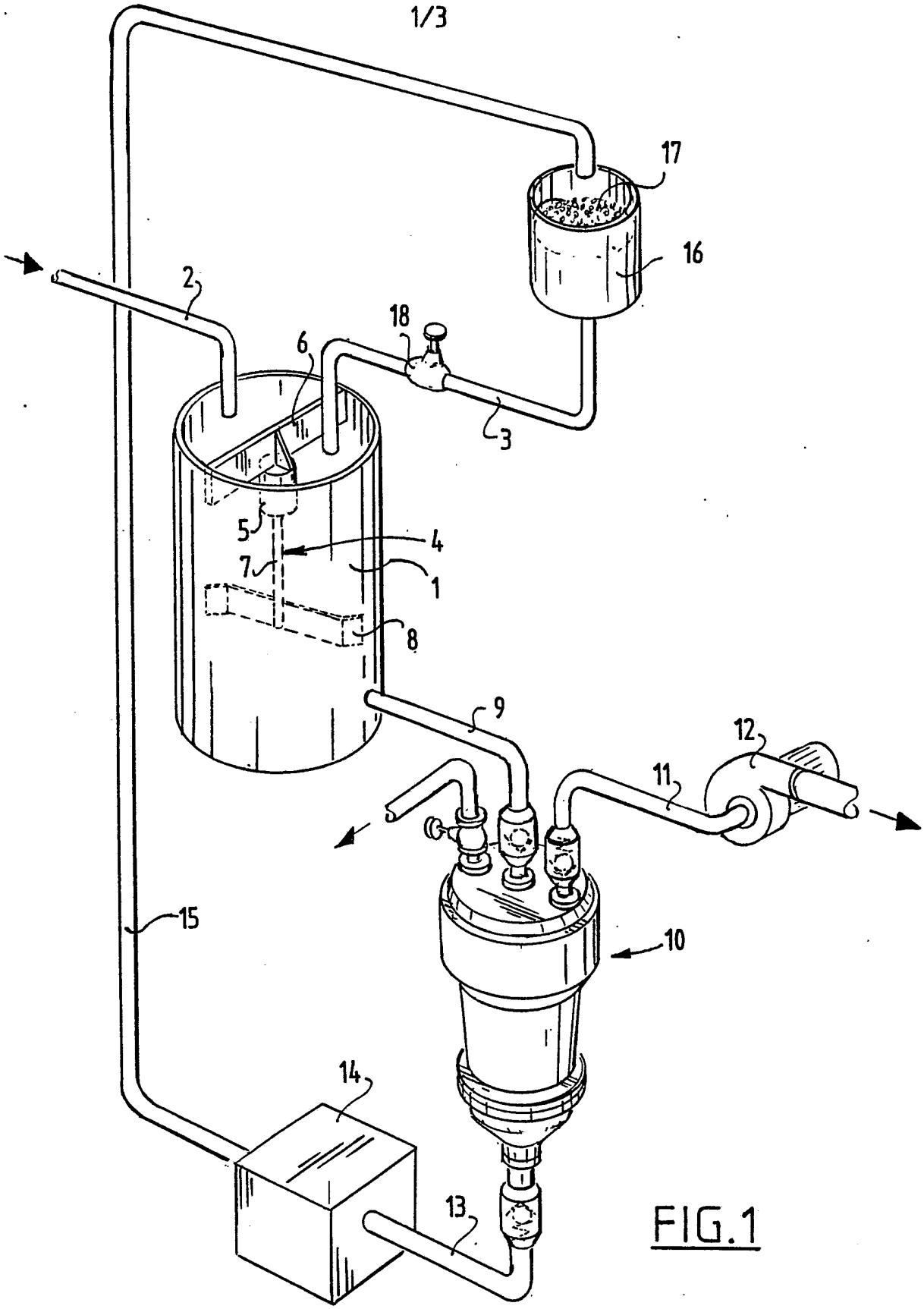

FIG.1

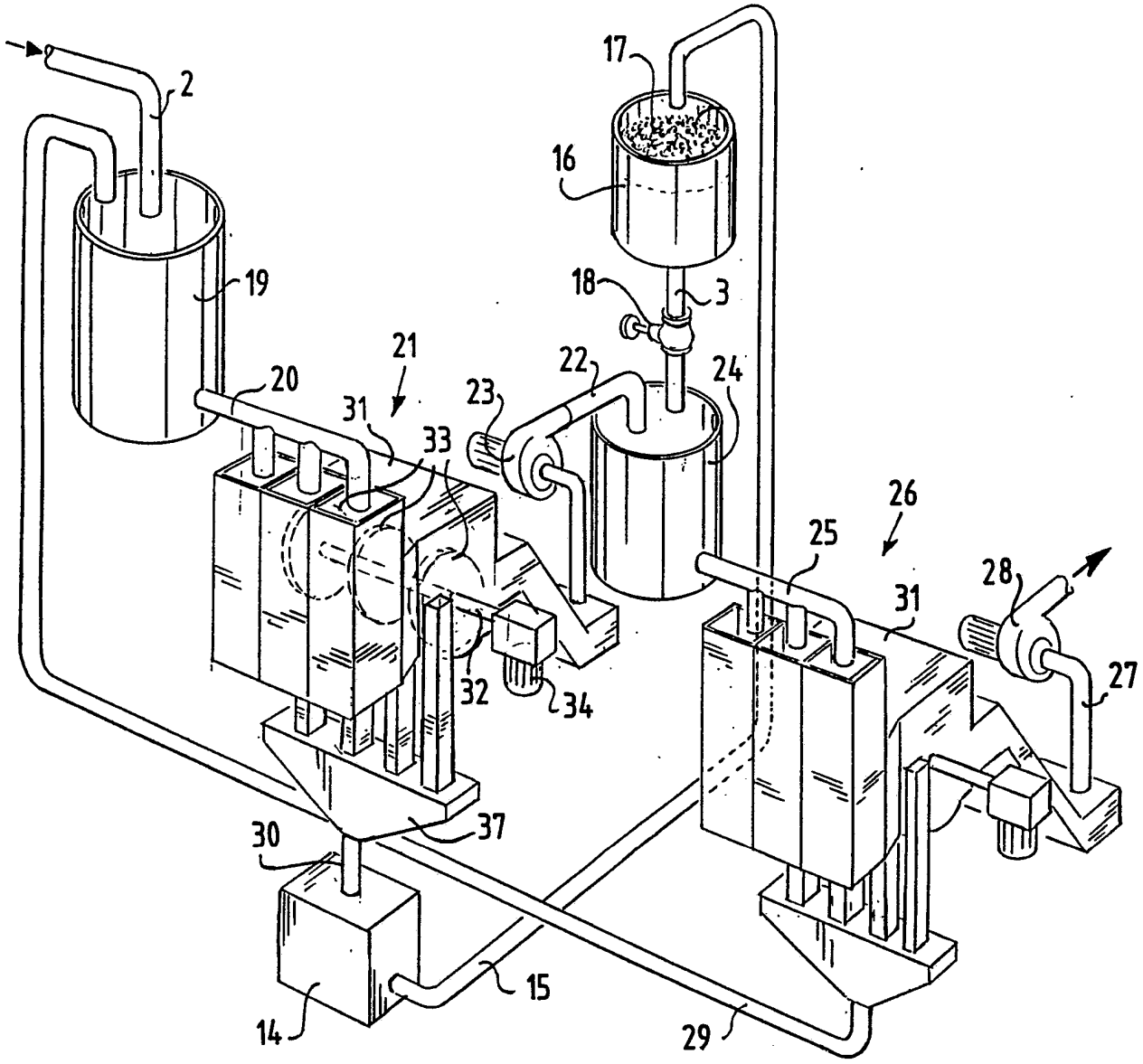

FIG.2

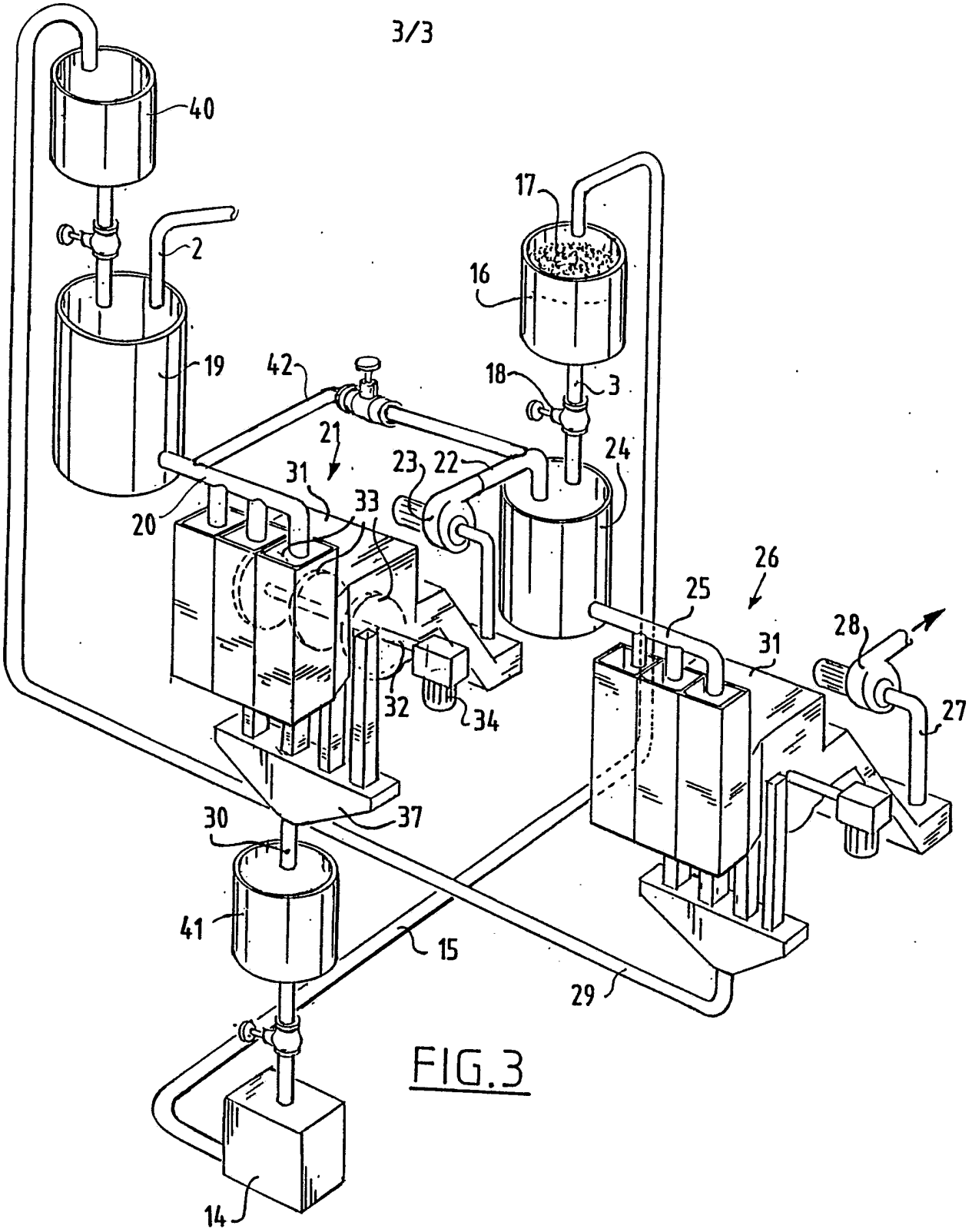
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FIG.3

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 93/00082

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C02F1/42; B01J47/10; B01J47/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C02F ; B01J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
Y	NL,A,7 307 704 (VISCOSE DEVELOPMENT CO.) 4 December 1973 see page 10, paragraph 3 - page 14, paragraph 1; figures 1,2 ---	1,4,6-8
Y	NL,A,7 702 147 (CLARKE CHAPMAN) 30 August 1977 see page 12, paragraph 7 - page 18, paragraph 2; figure 7 see page 19; claims 5-6 ---	1,4,6-8
A	BE,A,668 584 (A.PRIGOGINE) 21 February 1966 see page 4, line 29 - page 7, line 20 ---	1,3,8
A	DE,A,1 417 619 (ASAHI KASEI KOGYO) 2 January 1969 ---	

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
23 JUNE 1993	-5. 07. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	WENDLING J.P.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 450 (C-547) & JP,A,63 175 686 (NIPPON DENKI KANKYO) 25 November 1988 see abstract -----	1,3

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

NL 9300082
SA 72309

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
NL-A-7307704	04-12-73	GB-A- 1436547	19-05-76
		AU-B- 507954	06-03-80
		AU-A- 5640873	05-12-74
		BE-A- 800402	01-10-73
		CA-A- 1005585	15-02-77
		DE-A- 2328086	13-12-73
		FR-A,B 2186289	11-01-74
		JP-A- 50043054	18-04-75
		US-A- 4154675	15-05-79
NL-A-7702147	30-08-77	GB-A- 1559809	30-01-80
		AU-B- 513508	04-12-80
		AU-A- 2271077	31-08-78
BE-A-668584	21-02-66	None	
DE-A-1417619	02-01-69	GB-A- 959227	
		US-A- 3207577	